# ANNUAL REPORT OF THE DIRECTOR OF THE FIXED NITROGEN RESEARCH LABORATORY

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UNITED STATES DEPARTMENT OF AGRICULTURE,
FIXED NITROGEN RESEARCH LABORATORY,
*Washington, August 6, 1924.*

SIR: I have the honor to transmit herewith the annual report of the Fixed Nitrogen Research Laboratory for the fiscal year ended June 30, 1924.

Respectfully,

F. G. COTTRELL, *Director.*

Hon. HENRY C. WALLACE,
*Secretary of Agriculture.*

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## INTRODUCTION

This is the fifth full year of operation of the laboratory and its third under the Department of Agriculture. The work of the year has, for the most part, been a direct continuation of the same problems discussed in their general aspects in last year's report. An effort has therefore been made in preparing the present report to confine the presentation chiefly to those aspects of the work which are either new or have taken on special significance as the investigations have progressed.

## THE DIRECT SYNTHETIC AMMONIA PROCESS

During the past year the investigation of the direct synthetic ammonia process was primarily concerned with the technical adaptation of the catalysts developed by the laboratory. The most satisfactory utilization of these catalysts involved difficult problems in gas purification and circulation at high pressures. Satisfactory solutions were found, however, which have resulted in a greatly simplified process. With these improvements, the cost per annual ton of ammonia production has been decreased about 50 per cent over former estimates, as, for example, in "Report on the Fixation and Utilization of Nitrogen," War Department Document 2041, published in 1922.

The progress made during the past year in the development of the technical details of the direct synthetic ammonia process from both chemical and mechanical aspects has won for this laboratory the interest and attention of the industry and thus made it possible for the laboratory to cooperate actively with various manufacturers of ammonia. One manufacturer in particular has worked closely with the laboratory staff in the production of detailed drawings for a 3-ton-per-day plant to be located in the West, where cheap water power is available for generating electrolytic hydrogen. These drawings were commenced last January and are now very nearly completed. Fabrication of materials has been started and commencement of operation is expected during the coming winter. In the case of several other ammonia plants aid has been given regarding the design or redesign of special equipment and in the preparation of catalysts.

In connection with the work of design it was necessary to carry on some engineering research. This was particularly true of pump packing, valves, gaskets, and means of closing the ends

of the converter. The device developed by the laboratory for this latter purpose, among other things, particularly lends ease and facility to dismantling the converter.

In cooperation with the manufacturers several compressors and blowers have been tried out with the view to securing the most efficient equipment for the special requirements of the problem.

The investigation of ammonia catalysts was extended to higher pressures than have been employed heretofore. At 1,500 atmospheres, for example, nearly 80 per cent of the gas mixture was converted to ammonia on a single pass through the catalyst, and this under condit ons which are of technical significance. Endurance tests on these same catalysts at high pressures reveal a performance which has not seemed possible with the contact materials and procedures reported by other investigators.

Closely associated with the investigat on of the direct synthetic method for fixing atmospheric nitrogen has been the study of practical methods of hydrogen production. Any further reduction in the cost of ammonia is most likely to be the result of a lowering in the cost of producing highly pur'fied hydrogen. For large-scale industrial purposes the utilization of water gas, natural gas, and by-product coke-oven gas probably offers the most fruitful field for exploitation. For an independent industry the water-gas method 's naturally to be preferred. Furthermore, its technical development has progressed further than that of any of the other methods. For immediate needs, therefore, the attention of this laboratory has been largely directed toward the production and purification of water-gas hydrogen.

The water-gas method for hydrogen involves the use of a catalyst for converting carbon monoxide and steam into hydrogen and carbon dioxide. During the past year substantial progress has been made in the development of catalysts for this reaction. Their performance under semitechnical conditions is to be investigated during the coming year. This more complete study is being made possible by the installation of a small water-gas plant and purification system, designed to supply a nitrogen-hydrogen gas mixture to a one-quarter ton synthetic plant operated during the past year on electrolytic hydrogen.

The removal of carbon dioxide from the water-gas hydrogen has represented an appreciable item in the cost of purifying hydrogen from this source. Several absorption methods for carbon dioxide have been under investigation. One of these has given very encouraging results and may effect a considerable simplification in the purification process.

A study of the mechanism of catalytic action has led to some interesting observations which are soon to be published. These investigations are opening up new catalyst possibilities which may lead to marked improvements in the performance of contact agents, particularly for the ammonia synthesis.

## CYANIDES

That nitrogen is fixed in the form of cyanides in the operation of the blast furnace has long been known. There is very little information, however, on the extent of cyanide formation and the feasibility of its recovery. During the past year a cooperative study was begun with the Bureau of Mines on this problem. Information of a preliminary nature was obtained on the concentration of cyanide at various levels in one blast furnace. Special experimental equipment has been designed and constructed to determine definitely the extent of cyanide formation under various operating conditions and the feasibility of cyanide recovery. This investigation is being continued.

Investigations were continued on the fixation of nitrogen by the soda ash-carbon reaction. Work was completed which appears to definitely establish the mechanism of the reactions in cyanide formation, and information was obtained on the thermal stability of sodium cyanide and sodium carbide. These results are proving of value not only in analyzing the difficulties in the commercial operation of the sodium-cyanide process, but also in the study of cyanide formation in the blast furnace. They are also suggestive of methods of improving the cyanide process as now operated. The results of these studies are being prepared for publication.

## NITRIDES

The fixation of n'trogen in the form of aluminum nitride from which pure alumina—for use in the manufacture of aluminum—and ammonia can readily be obtained has been a subject of extensive invest'gations in this country and abroad, but a satisfactory process has not yet been developed. This process is to be regarded essen-

tially as one for the production of pure alumina with ammonia as a by-product, or, in other words, the ammonia thus obtained would bear somewhat the same relation to aluminum as that of coke-oven ammonia to steel. During the past year the laboratory began an investigation of this problem along what appears to be a more promising line of attack than that on which most of the previous work has been spent. The method involves the production of an alloy of aluminum, its nitrification, and the hydrolysis of the nitrified product, thus producing ammonia and alumina. The nitrification of various aluminum alloys was studied and some information obtained on the hydrolysis of the material. Further investigation is necessary to determine the value of the method, and the work is being continued.

A short study was made of the preparation and properties of phosphorus nitride. It was found that this compound, which contains the highest possible concentration of two necessary fertilizer elements, nitrogen and phosphorus, is so slowly decomposed in the soil that it is not suitable for application as such to the soil. The compound can be decomposed by suitable autoclave treatment, however, yielding ammonia and phosphoric acid, but no feasible method has as yet been found for its commercial production.

## CYANAMIDE

Investigations on the utilization of calcium cyanamide as a fertilizer, both for use as such and after conversion to urea-containing materials, were made during the past year. Some information was obtained on the fertilizer value of mixtures of calcium cyanamide and basic phosphate through field experiments carried on cooperatively with the Bureau of Plant Industry. The results as yet obtained can not be regarded as conclusive and the experiments are being continued.

A number of proposed processes for producing urea and urea-containing mixtures from calcium cyanamide suitable for fertilizer use were investigated and information was obtained on which an estimate of their value can be based. In this connection a method was developed on a laboratory scale for the production of cyanamide in a free state ($H_2CN_2$), which appears to have important advantages over other methods which have been reported. This method, which also appears adaptable to large-scale operation, will, if found commercially satisfactory, be of decided importance to the cyanamide industry in furnishing the link between the raw material and the many nitrogen compounds, including urea, which can be made from cyanamide in the free state.

In connection with the cyanamide process, a brief study was made of the formation of carbide, since the principal cost of fixing nitrogen by this process is in the manufacture of the carbide. Attention was directed in particular to the feasibility of producing carbide from lime-carbon mixtures at temperatures below the fusion point of the charge. Carbide formation was found to occur at temperatures far below the fusion point, but satisfactory yields could not be obtained under practical conditions. The investigations on the cyanamide process proper, initially undertaken by the laboratory, have now been concluded and the principal results published.

## NITROGEN FIXATION BY MICRO-ORGANISMS

That bacteria in the soil fix enormous quantities of nitrogen is well known, but the manner in which they so successfully do so at atmospheric temperature and pressure has not been discovered. With the ultimate aim of gaining some idea of the mechanism by which bacteria fix nitrogen, various elements which effect the growth and fixation by these organisms have been studied during the year. The importance of certain plant extracts in stimulating the growth of *Bacillus radicicola* has been of special consideration, with a view to determining the constituent in the extract primarily responsible for the marked stimulation. This investigation is being continued.

## OXIDES OF NITROGEN AND NITRIC ACID

Investigations on the recovery of oxides of nitrogen from gaseous mixtures obtained in the oxidation of ammonia and in the arc process of nitrogen fixation were continued. Additional information was obtained on the use of silica gel for this purpose, and through cooperation with the department of chemical engineering, Yale University, special equipment has been designed and set up for the opera-

tion on a small scale of a process of recovery which appears to be promising. It is expected that definite information on the feasibility of the process will be obtained during the present year.

Nitric acid is not only the principal form of fixed nitrogen required in the manufacture of explosives, but it is finding increased use in the chemical industry and in the manufacture of fertilizer salts. During the past year a laboratory study was made to determine the conditions under which concentrated oxides of nitrogen can be directly converted into nitric acid of practically any desired concentration. This investigation, while not entirely complete, has established quite definitely the conditions for the production of acid ranging in concentration up to 94 per cent. Since nitric acid is very corrosive to most metals, a series of corrosion tests on various metals and alloys was made under a variety of conditions to ascertain what materials are suitable for the construction of equipment required in the production of acid by the synthetic process and for handling the acid.

## ACTIVE NITROGEN AND CHEMICAL REACTIVITY

While much of the effort of the laboratory is directed toward the investigation of problems which bear directly on the industrial development of the fixation and utilization of atmospheric nitrogen, some effort is spent in a study of the fundamental scientific principles underlying these problems.

It is of prime importance to determine the various conditions under which nitrogen can be made reactive and thus be obtained in chemical combination. The nitrogen molecule can not take part in a chemical reaction until it has been properly disturbed or excited. The laboratory has studied the various stages and modes of excitation of the molecules of nitrogen, oxygen, and of various other gases in order to render them chemically active.

In addition, the properties of the excited molecules of oxygen and nitrogen which are necessary to the formation of ozone and chemically active nitrogen have been studied. The processes of reversion of these unstable substances to the normal nitrogen and oxygen have also been investigated. The work done on the explosive decomposition of ozone has a direct application to the formation of nitric oxide in the arc process for nitrogen fixation.

It is expected that definite and important conclusions regarding the chemical reactions involving nitrogen will follow from further work along these lines.

## COOPERATIVE WORK WITH DEPARTMENT OF COMMERCE

The laboratory has cooperated with the Department of Commerce in the survey of the nitrogen problem which is being made by the Bureau of Foreign and Domestic Commerce of that department, in connection with an investigation of essential raw materials now produced largely abroad under monopoly control. At the beginning of the year two members of the laboratory staff spent three months abroad, collecting technical and economic information on the nitrogen problem, with particular reference to the fixation and utilization of atmospheric nitrogen. The countries visited in this study were Germany, France, Italy, Switzerland, Czechoslovakia, Austria, Belgium, Holland, England, Norway, Sweden, and Denmark.

A part of the information thus obtained, together with information on other phases of the subject obtained through other channels, is being published by the Bureau of Foreign and Domestic Commerce, as a series of bulletins under the title of "Nitrogen Survey." For the information of those interested these reports are listed below and may be obtained from the Chemical Division, Bureau of Foreign and Domestic Commerce, Department of Commerce.

PART I. The Cost of Chilean Nitrate. By H. Foster Bain and H. S. Mulliken. Trade Information Bulletin No. 170. 66 pp. Issued January 7, 1924.

PART II. General Review of the Nitrogen Situation in the United States. By Harry A. Curtis. Trade Information Bulletin No. 226. 63 pp. Issued May 5, 1924.

PART III. The Air-Nitrogen Processes. By J. M. Braham. Trade Information Bulletin No. 240. 41 pp. Issued June 16, 1924.

PART IV. The Nitrogen Situation in Various Countries in Europe. By Harry A. Curtis and Frank A. Ernst. (In course of preparation.)

PART V. Nitrogen Bibliography. (In course of preparation.)

## LIST OF PUBLICATIONS FROM THE FIXED NITROGEN RESEARCH LABORATORY

[Chronologically arranged for the fiscal year 1923–24]

Deterioration of Steel and Wrot Iron Tubes in Hot Gaseous Ammonia. By J. S. Vanick. Trans. Amer. Soc. for Steel Treating IV, No. 1, July, 1923.

Analysis of Hydrogen for Traces of Nitrogen. By R. L. Dodge. Jour. Amer. Chem. Soc., 45, No. 7, July, 1923.

Preparation of Dicyanodiamide from Calcium Cyanamide. By H. C. Hetherington and J. M. Braham. Jour. Ind. and Eng. Chem., 15, No. 10, October, 1923.

Determination of Nitrate Nitrogen in the Presence of Cyanamide and Some of its Derivatives. By K. D. Jacob. Jour. Ind. and Eng. Chem., 15, No. 11, November, 1923.

The Synthetic Ammonia Process of Nitrogen Fixation. By A. T. Larson. Army Ordnance Journal, IV, No. 21, November and December, 1923.

The Ammonia Equilibrium. By A. T. Larson and R. L. Dodge. Jour. Amer. Chem. Soc., 45, No. 12, December, 1923.

Field Experiments with Atmospheric Fertilizers. By F. E. Allison and J. M. Braham (Fixed Nitrogen Research Laboratory) and J. E. McMurtrey (Bureau of Plant Industry). U. S. Dept. Agr. Bul. No. 1180, January, 1924.

The Ammonia Equilibrium at High Pressures. By A. T. Larson. Jour. Amer. Chem. Soc., 46, No. 2, February, 1924.

The Electrical Conductivity of Active Nitrogen. By S. Karrer, C. S. Fazel, and B. V. Cassen. Physical Review, 23, February, 1924.

The Preparation and Chemical Nature of Calcined Phosphate. By E. W. Guernsey and J. Y. Yee. Jour. Ind. & Eng. Chem., 16, No. 3, March, 1924.

Chemical and Biological Studies with Cyanamid and Some of its Transformation Products. By K. D. Jacob, F. E. Allison, and J. M. Braham. Jour. Agr. Research, 28, No. 1, April, 1924.

Common Sense and the Problem of Nitrogen Fixation. By F. G. Cottrell. Tech. Engineering News, Mass. Inst. Tech., May, 1924.

Nitrogen Survey, Part III, The Air-Nitrogen Processes. By J. M. Braham. Dept. of Com. Trade Information Bulletin No. 240, June, 1924.

The Mechanism and Thermochemistry of the Reaction between Calcium Carbide and Nitrogen. By H. J. Krase and J. Y. Yee. Jour. Amer. Chem. Soc., 46, No. 6, June, 1924.

A Method for the Determination of Calcium Carbide. By J. Y. Yee and H. J. Krase. Jour. Amer. Chem. Soc., 46, No. 6, June, 1924.

Effect of Cyanamide and Related Compounds on the Number of Microorganisms in the Soil. By F. E. Allison. Jour. Agr. Research, 28, No. 11, June, 1924.

The Nitrification of Phosphorus Nitride. By F. E. Allison. Jour. Agr. Research 28, No. 11, June, 1924.

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